

# PATENT SPECIFICATION

(11) 1 528 623

1 528 623

- (21) Application No. 40048/75 (22) Filed 30 Sept. 1975  
 (31) Convention Application No. 7412370  
 (32) Filed 1 Oct. 1974 in  
 (33) Sweden (SE)  
 (44) Complete Specification published 18 Oct. 1978  
 (51) INT CL<sup>2</sup> C10J 3/54 C01B 2/22  
 (52) Index at acceptance  
 C5E G11 G13 G4F G5 G7B

(19)



## (54) A PROCESS AND APPARATUS FOR GASIFICATION OF CARBONACEOUS MATERIALS

(71) We, STORA KOPPARBERGS BERGSLAGS AKTIEBOLAG, a Swedish joint stock company, of Falun, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for converting carbonaceous materials to a gas mixture containing CO and H<sub>2</sub> by gasification of finely divided solid and/or liquid carbonaceous materials. By solid carbonaceous materials are understood, for instance, finely divided coke, anthracite, black coal or brown coal, or mixtures of two or more of these materials. By liquid carbonaceous materials are understood hydrocarbons liquid at normal ambient temperature, as, for example, fuel oils, tar oils and topped crude.

According to one aspect of the invention we provide a method for converting carbonaceous material to a gas mixture containing CO and H<sub>2</sub> by gasification at elevated temperatures, which comprises gasifying the carbonaceous material, which if solid is of grain size <3 mm, in a circulating fluid bed maintained in a vertically elongated reactor, gasifying medium comprising gas containing molecular oxygen and water vapour, and the carbonaceous material, being supplied to the fluid bed through the wall of the reactor at a controlled flow rate, while the fluidization of the bed in the lower part of the reactor is maintained by feeding into the bottom of the reactor at a controlled flow rate non-oxidizing or substantially non-oxidizing gas, the gasifying medium being introduced into the reactor remote from the bottom thereof subdivided into several part flows, maintaining the reaction temperature by adjusting the percentage of molecular oxygen in the gasifying medium, and discharging bed material from the bottom part of the reactor at a rate such as to maintain a predetermined ratio of ashes in the reactor.

We describe below an apparatus used for carrying out the process of the invention and

comprising a vertically arranged refractory-lined reactor, the upper part of which is connected to separation means for separating solid material from gas passing from the reactor, conduits for returning the solid material to the reactor, first openings in the bottom of the reactor for the introduction of fluidizing gas, second openings in the wall of the reactor for the introduction of a gas containing molecular oxygen and water vapour in the form of jets that are directed inwardly away from wall inlets for solid material and a discharge conduit at the bottom of the reactor.

The grain size of solid carbonaceous material used in our method is preferably less than 1 mm; gasification may be carried out at superatmospheric pressure. The gasification takes place in a circulating fluid bed (for definition see for instance Chemical Engineering Progress, Vol. 67, February 1971, pp. 58—63; L. Reh: Fluidized Bed Processing) containing fine-grained solid material and maintained in a vertically elongated reaction zone, to which the carbonaceous materials and the gasifying medium are supplied at controlled flow rates. The fine-grained solid material in the fluid bed may consist of the fine-grained solid materials, supplied, pyrolysis residues and ashes from the carbonaceous solid materials or possibly an inert material, for instance Al<sub>2</sub>O<sub>3</sub>. The fluidization in the lower part of the reactor is maintained by introducing a non-oxidizing or substantially non-oxidizing gas generally containing less than 10% O<sub>2</sub> by volume, for instance a partial flow of the gas mixture produced containing CO and H<sub>2</sub>, into the part of the zone below the entrance of the gasifying medium, usually the bottom of the reactor. In the bed fluidized in this manner the gasifying medium is supplied subdivided into a plurality of part flows, so as to be rapidly mixed with the by-flowing mixture of gas and solid materials, local overheating by the partial combustion with the oxygen of the gasifying medium thus being limited and controlled.

In order to prevent deposits on the wall of the reactor local overheating adjacent to the

wall must be avoided, suitably by directing the flows of gasifying medium away from the wall. Suitably, the angle between the directions of flow and wall should be at least  $10^\circ$ . Moreover, the flows must not be so strong as to penetrate through the bed and come close to an opposite wall; this can usually be avoided by selecting a sufficient number of small partial flows. These are suitably distributed around the zone i.e. circumferentially in one array or two or more vertically spaced arrays. The temperature in the reaction zone is maintained at the desired level i.e. usually  $800-1200^\circ\text{C}$ ., by controlling the percentage of oxygen gas of the gasifying medium.

A mixture of gas and solid materials leaves the upper part of the reaction zone and is subjected to separation. Solid material thus separated is returned to the lower part of the zone. The hot gas purified from solid materials consists essentially of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$ . After cooling and at the same time recovering part of its physical heat content, for instance for generation of steam for the gasification, and after washing and absorption in a known way of the major part of its  $\text{CO}_2$ -content, a gas mixture, generally of high quality, consisting of  $\text{CO}$  and  $\text{H}_2$  is obtained. This mixture may advantageously be used as a synthesis gas and/or after methanization as a synthetic natural gas.

In order to maintain an acceptable content of ashes formed during the gasification of the solid carbonaceous materials in the reaction zone, a controlled flow rate of bed material is discharged from the bottom part of the reaction zone. The ash content allowable is dependent on the characteristics of the ashes and of the coal. In favourable cases an ash content of above 90% may be tolerated, which means that only a few percents of the carbon in the feed will leave with the ashes. In certain cases the ash content must be kept lower and then it may become desirable to utilize the relatively higher carbon content of the ashes in some way.

In an embodiment of the invention there may be included the steps of sulphur purification of the fuel and possibly recovery of the sulphur. The carbonaceous materials suitable for the process often have high contents of sulphur. In this case  $\text{CaO}$ -containing materials are supplied to the reaction zone. The sulphur liberated as  $\text{H}_2\text{S}$  from the supplied carbonaceous materials is then bound to  $\text{CaO}$  in the form of  $\text{CaS}$ . A good sulphur removal is obtained if the  $\text{CaO}$ -content of the reaction zone is maintained at a higher level than its  $\text{CaS}$ -content. This is achieved by controlling the supply of  $\text{CaO}$ -containing material and by discharging a controlled flow rate of bed materials from the bottom part of the reaction zone. In this connection it is suitable to remove ashes and sulphur from the latter flow and thereafter return it to the reaction zone.

The  $\text{CaO}$ -containing material may either be fine-grained as the rest of the bed materials, i.e.  $<$  about 3 mm, and may then be supplied in any part of the reaction zone. However, it may also be coarse-grained, i.e.  $>$  about 3 mm and up to about 10 mm. Then it will not completely fluidize but will sink through the bed. In this case it should, therefore, be added at the top of the reaction zone. After discharge at the bottom it may be separated from the rest of the bed materials by sifting, freed from sulphur and recirculated.

Ashes may be removed from discharged bed materials by two principally different methods, below called the mechanical method and the magnetic method.

According to the mechanical method the operative temperature in the reaction zone is sufficiently high for the ashes to soften and agglomerate. Since ashes only agglomerate with ashes and not with coke, the ash agglomerates grow progressively to such a size that they settle towards the bottom of the reaction zone. When discharging bed materials therefrom, there is obtained a mixture of materials containing ash agglomerates which in view of their size may be separated mechanically, for instance by sifting, and then dumped. If  $\text{CaO}$ -containing material is added for sulphur purification it should be fine-grained so as to end up in the fraction freed from ashes. The rest of discharged bed material is then in a known way freed from the major part of its sulphur content and returned to the reaction zone.

The mechanical method for removing the ashes works satisfactorily when the solid carbonaceous material supplied to the reaction zone has a uniform composition. In view of the fact that most the compositions of such materials can vary greatly comprehensive arrangements for obtaining a fairly uniform mixture for discharge are desirable, for instance bedding i.e. stratifications to form thin layers or beds of different material to form a composite bed having a definable overall composition.

According to the magnetic method for removing the ashes from the discharged bed material the gasification takes place just below the softening temperature of the ashes in the solid carbonaceous material feed. The bed material discharged from the bottom part of the reaction zone is in this case cooled below the Curie point of the iron compounds of the ashes, the material being then magnetically fractionated. The cooling is generally carried out to allow for heat recovery, suitably using the gasifying medium as a coolant. In the fractionation a magnetic fraction is obtained essentially containing ashes the iron content of which, due to the reducing conditions in the lower part of the reaction zone, partly consists of  $\text{Fe}$  or  $\text{Fe}_3\text{O}_4$ . This fraction is

dumped. The non-magnetic fraction obtained, essentially containing coke and CaO/CaS-containing components, is then freed from its sulphur content in a known manner and is then returned to the reaction zone.

The magnetic method for removing the ashes operates satisfactorily provided that the  $\text{Fe}_2\text{O}_3$ -content of the ashes of the supplied solid carbonaceous material is  $>5\%$ . This is the case with most of the black and brown coal types, in view of which the magnetic method has been found to be essentially independent of normal variations in the characteristics of the solid carbonaceous material supplied.

The flow of bed material discharged from the bottom part of the reaction zone is controlled in connection with the magnetic ash separation in such a manner that the ash content of the zone is maintained at a level permitting undisturbed operation. The level is dependent on the characteristics of the ashes and must be determined by trial and error for each operation.

Accumulation in the system of certain substances such as  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , found in small contents in the non-magnetic fraction may be avoided by dumping a minor part ( $<10\%$ ) of the non-magnetic fraction. Ca-content lost hereby is compensated by supplying to the fraction a balanced flow of external CaO-containing material, such as limestone, dolomite or burned dolomite. Since in principle Ca circulates within the system, the CaO-content in the reaction zone is maintained at approximately the desired level by intermittent over- or underfeeding the external CaO-containing material.

Sulphur can be removed in several ways from the discharged bed material from which ashes have been removed. A particularly suitable method is to bring the material at an elevated pressure and temperature into contact with a gas mixture containing  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . This will convert the CaS-content to  $\text{H}_2\text{S}$  and  $\text{CaCO}_3$ . In a Claus process  $\text{H}_2\text{S}$  is converted to elementary sulphur which can be marketed, whereas the formed  $\text{CaCO}_3$ -containing component together with the coke content of the material is returned to the reaction zone. In our process  $\text{CaCO}_3$  is thermally decomposed at the high operating temperatures to CaO which binds further amounts of sulphur.

In a particularly advantageous embodiment of the invention the  $\text{CaCO}_3$  formed during the removal of sulphur is decomposed in a separate operation in a venturi bed by means of the hot gas that after cleaning from dust issues from the upper part of the reaction zone.  $\text{CaCO}_3$  is thermally decomposed to CaO and the mixture of gas and solid material obtained is separated, the solid material (coke+CaO-containing component) being returned to the reaction zone. This embodiment provides sul-

phur purification in two steps and therefore results in an extra low sulphur content in the gas produced.

An embodiment of the invention will now be further described with reference to the appended drawing which shows schematically an apparatus for circulating fluid bed gasifications.

The apparatus illustrated comprises of a refractory-lined shaft 1 including a vertically elongated reaction zone and being connected at its top opening to separation means 2, 3 from which return conduits 4, 5 for solid material lead back to the shaft. In the bottom of the shaft there are orifices 6 for introduction of fluidizing gas through the bottom surface of the zone. In the wall of the shaft there are orifices 7 for the introduction of gasifying medium in the form of jets directed inwardly away from the wall and inlets 8, 9 for the supply of carbonaceous material and for CaO-containing material respectively. At the bottom of the shaft there is also a discharge conduit 10 for solid materials. From the separation means 2, 3 the formed gas containing  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$  passes through a conduit 11 to a cooling and purifying plant 12 consisting of a waste heat boiler 13, where an essential part of the physical heat content of the gas is recovered in the form of steam, a water scrubber 14, where the gas is washed with cold water to remove its contents of dust and water vapour, and a device for absorption of carbon dioxide 15, where the gas is brought into contact with a suitable absorption solution (for instance  $\text{K}_2\text{CO}_3$ ) thus removing its  $\text{CO}_2$ -content. The orifices 7 should preferably lie at a level between the middle of the reaction zone and about half a meter above the orifices 6.

Steam 16 is passed from the boiler 13 to the inlet orifices 8 for carbonaceous material, and also in mixture with oxygen 17 to a heat exchanger 18, from which the mixture through a conduit 19 passes to the inlet orifices 7 for the gasifying medium. Part of the purified gas 20 passes through a conduit 21, 22 to the inlet orifices 6 in the bottom of the shaft and operates there as a fluidizing gas in the part of the reaction space located below the inlet orifices 7 for the gasifying medium. Another part passes through a branch conduit 23 to a fluid bed of conventional type 24 for the solid material issuing from the bottom of the shaft through conduit 10. This material is subjected to heat exchange with the entering gasifying medium by means of the heat exchange surfaces 18. After cooling below the Curie point the solid material is magnetically separated by means of the magnet separator 25. This results in a magnetic fraction 26 essentially consisting of ashes, the iron content of which is partly present as  $\text{Fe}$  or  $\text{Fe}_3\text{O}_4$ . This fraction is dumped.

The non-magnetic fraction 27 is brought into contact with a gas mixture containing  $H_2O$  and  $CO_2$ , known manner in a fluid bed 28 at an increased temperature and increased pressure. This results in removal of the major part of the sulphur content of the fraction in the form of  $H_2S$  35 which in a subsequent Claus process 29 is converted to elementary sulphur 30.

The content of bed materials in the sulphur removal bed 28 is maintained constant by controlled discharge of bed material 31. This consists essentially of coke and  $CaCO_3$ -con-

taining component and is returned to the reaction zone after diversion and dumping of a minor part 32 and replacement of lost  $CaO$  by controlled addition of external  $CaO$ -containing material 33, such as burned and unburned limestone and dolomite.

#### Example

As a practical example of the method according to the above description the following data may be given, The reactor has an internal diameter of 6.6 meters and a height of 25 meters.

	Flow of material	t/h	NM <sup>3</sup> /h	Temperature °C		
	Coal (8)	65		200		
	Gas (11)		188,000	900		
	Steam (16)	33.4		290		
30	Oxygen (17)		39,000	200		
	Gas (22)		19,000	20		
	Ashes (26)	6.1		350		
	Coal analysis	C	CH <sub>1.7</sub>	O	Moisture	Ashes
		45.3	39.0	4.8	2.5	8.4 %
35	Gas analysis (11)	CO	CO <sub>2</sub>	CH <sub>1.7</sub>	H <sub>2</sub> O	H <sub>2</sub>
		49.9	5.5	1.1	5.7	37.8 %

The gas pressure within the bed is about 5 ats. The steam quantity from the boiler (13) is 76 t/h, 33.4 t/h of which is produced as saturated steam at 290°C and is fed into pipe (16), the rest being produced as overheated steam at 450°C and by not illustrated pipes fed, for instance, to preheating of oxygen (17) or water supply to the boiler (13).

About 10% of the produced gas quantity passing through pipe (11) is recirculated through pipe (22).

The bracketed numbers above refer to the drawing.

#### WHAT WE CLAIM IS:—

1. A process for converting carbonaceous material to a gas mixture containing  $CO$  and  $H_2$  by gasification at elevated temperatures, which comprises gasifying the carbonaceous material, which if solid is of grain size <3 mm, in a circulating fluid bed maintained in a vertically elongated reactor, gasifying medium comprising gas containing molecular oxygen and water vapour, and the carbonaceous material, being supplied to the fluid bed through the wall of the reactor at a controlled flow rate, while the fluidization of the bed in the lower part of the reactor is maintained by feeding into the bottom of the reactor at a controlled flow rate non-oxidizing or substantially non-oxidizing gas, the gasifying medium being introduced into the reactor remote from the bottom thereof subdivided into several part flows, maintaining the reaction temperature by adjusting the percentage of molecular oxygen in the gasifying

medium, and discharging bed material from the bottom part of the reactor at a rate such as to maintain a predetermined ratio of ashes in the reactor.

2. A process in accordance with Claim 1, carried out at elevated pressure.

3. A process in accordance with Claim 1 or 2, using solid carbonaceous material of grain size <1 mm.

4. A process according to any one of Claims 1 to 3, wherein the gas mixture containing  $CO$  and  $H_2$  is cooled in a waste heat boiler to produce steam.

5. A process according to any one of the preceding claims, wherein the gas mixture produced is freed from water and carbon dioxide.

6. A process according to any one of the preceding claims, wherein a partial flow of the produced gas is used for fluidization in the lower part of the reactor.

7. A process according to any one of the preceding claims, wherein  $CaO$ -containing material is supplied to the reaction zone for removing sulphur present in the carbonaceous material as  $CaS$ .

8. A process according to Claim 7, wherein the supply of  $CaO$ -containing material and the discharge of bed material are carried out in such a way that the content of  $CaO$  in the bed is higher than the content of  $CaS$ .

9. A process according to Claim 7 or 8, wherein the discharged bed material is subjected to separation into a fraction containing ashes and a fraction containing  $CaO/CaS$ .

10. A process according to Claim 9, wherein the CaO/CaS-containing component is heated under pressure with water vapour and CO<sub>2</sub>, the major part of its sulphur being converted to H<sub>2</sub>S, which is thereafter recovered.

11. An apparatus when used to carry out the process according to Claim 1 for converting carbonaceous materials to a gas mixture containing Co and H<sub>2</sub> by gasification at an elevated temperature, comprising a vertically arranged refractory-lined reactor, the upper part of which is connected to separation means for separating solid material from gas passing from the reactor, conduits for returning the solid material to the reaction reactor, first openings in the bottom of the reactor for the introduction of fluidizing gas, second openings in the wall of the reactor for the introduction of a gas containing molecular

oxygen and water vapour in the form of jets that are directed inwardly away from wall inlets for solid material and a discharge conduit at the bottom of the reactor.

12. A process according to Claim 1, substantially as described with reference to the accompanying drawing.

13. Apparatus according to Claim 11, substantially as described with reference to the accompanying drawing.

TREGEAR, THIEMANN & BLEACH,  
Chartered Patent Agents,  
Enterprise House,  
Isambard Brunel Road,  
Portsmouth PO1 2AN,  
and  
49/51 Bedford Row,  
London, WC1V 6RL.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

